PATENT ABSTRACTS OF JAPAN

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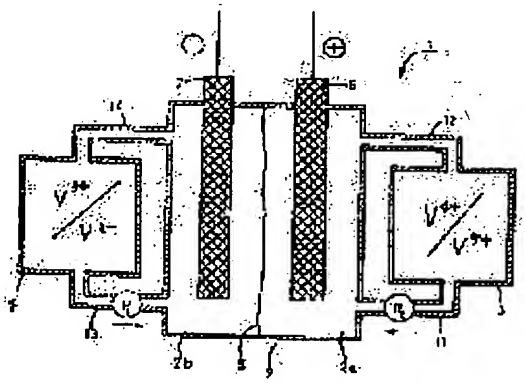
(54) OPERATING METHOD OF REDOX-FLOW CELL

(57)Abstract:

PURPOSE: To prevent deterioration of an electrode and lengthen the life of a cell by operating under a specified condition in a operating method for a redox-flow cell containing a specified positive active material.

CONSTITUTION: A redox-flow cell 1 contains a positive active material which changes from a first valency state (example: V4+) to a second valency state (example: V5+) in charge, and conducts reverse reaction in discharge, in a positive electrode. The cell 1 is operated so that when charge is finished, the positive active material in the first valency state is left in the electrolyte, and preferably the positive active material in the second valency state is 90% or less.



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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The operating method of the redox flow cell which changes from the 1st valence state to the 2nd valence state, and is characterized by operating so that the positive active material of said 1st valence state may remain into the electrolytic solution at the time of charge termination in a positive electrode in the operating method of the redox flow cell containing the positive active material which causes the reverse reaction at the time of discharge at the time of charge.
[Claim 2] The operating method of a redox flow cell according to claim 1 which operates so that the positive active material of said 2nd valence state may become 90% or less at the time of charge termination.
[Claim 3] The operating method of the redox flow cell according to claim 1 using vanadium ion as said positive active material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the operating method of the redox flow cell generally more specifically improved about the operating method of a redox flow cell so that degradation of an electrode might be reduced and the reinforcement of it could be carried out.
[0002]
[Description of the Prior Art] Drawing 1 is the outline block diagram of the redox flow cell proposed conventionally. The redox flow cell 1 is equipped with a cel 2, the positive-electrode liquid tank 3, and the negative-electrode liquid tank 4. The inside of a cel 2 is divided by the diaphragm 5 which consists of ion exchange membrane, one side constitutes positive-electrode cel 2a, and the other side constitutes negative-electrode cel 2b. In positive-electrode cel 2a and negative-electrode cel 2b, the positive electrode 6 or the negative electrode 7 is arranged as an electrode, respectively.
[0003] By the redox flow cell 1 shown in drawing 1 , the water solution of the ion from which a valence like iron ion and chromium ion changes, for example is stored in tanks 3 and 4, this is sent to the negotiation mold electrolysis cell 2 with Pump P, and an oxidation reduction reaction performs charge and discharge.
[0004] For example, when it considers as the solution of hydrochloric acid as positive active material, respectively, using Cr2+/Cr3+ as Fe3+/Fe2+ and a negative-electrode active material, the cell reaction in the two poles 6 and 7 of each oxidation reduction system becomes like the following formula.
[0005]
[Formula 1]

正極側 ： $Fe^{3+} + e \underset{\text{充電}}{\overset{\text{放電}}{\rightleftarrows}} Fe^{2+}$

負極側 ： $Cr^{2+} \underset{\text{充電}}{\overset{\text{放電}}{\rightleftarrows}} Cr^{3+} + e$

About 1-volt electromotive force is acquired according to the electrochemical reaction of an above-mentioned formula.
[0006] In JP,62-186473,A, the redox flow cell used as the sulfuric-acid solution, respectively is indicated using vanadium as positive active material as shown in drawing 2 , and a negative-electrode active material, and the cell reaction in this case becomes like the following formula.
[0007]
[Formula 2]

正極側 ： $V^{5+} + e \underset{\text{充電}}{\overset{\text{放電}}{\rightleftarrows}} V^{4+}$

負極側 ： $V^{2+} \underset{\text{充電}}{\overset{\text{放電}}{\rightleftarrows}} V^{3+} + e$

[0008]
[Problem(s) to be Solved by the Invention] by the decomposition reaction of what should just charge positive active material to what extent, and water when finishing charging positive active material, and the end of charge is approached, or -- as shown [since there was no clear guide,] in a degree type, oxygen occurred in the operating method of the conventional redox flow cell, as a result the electrode was oxidized to it, and there was a trouble of making an electrode tattering in it.
[0009]
[Formula 3]

$$OH^- \longrightarrow \frac{1}{2} O_2 + H^+ + 2e$$

Moreover, the liquid of the charge condition of positive active material had strong oxidizing power, and the more there was much charged positive active material, it was easy to carry out oxidation degradation of the electrode, as a result, the more it had the trouble that potential efficiency fell.
[0010] Moreover, when using vanadium ion for positive active material, compared with tetravalent vanadium, pentavalent vanadium has small solubility and tends to deposit. Therefore, there was a trouble that sludges increased in number as pentavalent vanadium increased.
[0011] This invention was made in order to solve the above troubles, and it aims at offering the operating method of the redox flow cell improved so that degradation of an electrode might be prevented and the reinforcement of it could be carried out.
[0012]
[Means for Solving the Problem] In a positive electrode, at the time of charge, this invention changes from the 1st valence state to the 2nd valence state, and takes for the operating method of the redox flow cell which contains the positive active material which causes that reverse reaction at the time of discharge. And in order to solve the above-mentioned trouble, it is characterized by operating so that the positive active material of the 1st valence state of the above may remain into the electrolytic solution at the time of charge termination.
[0013] According to the desirable embodiment of this invention, operation is performed so that the positive active material of the 2nd valence state of the above may become 90% or less at the time of charge termination.
[0014] According to the still more desirable embodiment of this invention, vanadium ion is used as the above-mentioned positive active material.
[0015]
[Function] Since operation of a redox flow cell is operated so that positive active material may not be charged 100%, oxygen evolution also decreases and degradation of an electrode decreases.
[0016] When charge of positive active material is especially made 90% or less, degradation of an electrode decreases. When vanadium ion is used for positive active material and charge is made 90% or less, a deposit can be further suppressed for vanadium ion.
[0017]
[Example] Hereafter, the example of this invention is explained.
[0018] Positive active material was compared about degradation of the electrode when charging to 90%, when charge was performed 100%, and it charged to 95%. Degradation of an electrode followed the value of potential efficiency as the rule of thumb. If conditions are the same, degradation of an electrode is because it appears in decline in potential efficiency.
[0019] It examined using the small cell as shown in drawing 2 using the three mols [/l.] example 1 vanadium 1 mol/l.-sulfuric acid. A result is shown in a table 1.
[0020]
[A table 1]

	９０％充電	９５％充電	１００％充電
充電前電極	８９．３％	８９．２％	８９．２％
充電後電極	８９．２％	８７．５％	８７．０％

The result of a table 1 shows that degradation of an electrode will tend to take place if it charges 100%. Moreover, when it is made 90% or less of charge, it turns out that degradation of an electrode decreases.
[0021] The small cell was produced using the two mols [/l.] example 2 vanadium 2 mol/l.-sulfuric acid, and the stability of pentavalent vanadium was investigated. Stability was investigated by performing a deposit trial at 50 degrees C. A result is shown in a table 2.
[0022]
[A table 2]

	９０％充電	１００％充電
析出具合	析出なし	析出した

It turned out that vanadium is so stable that there is little charge so that clearly from the result of a table 2.
[0023]
[Effect of the Invention] By the operating method of a redox flow cell, if it operates so that positive active material may not be charged 100%, degradation of an electrode can be decreased and can carry out reinforcement, as explained above.
[0024] Moreover, when vanadium ion is used for positive active material, a deposit of pentavalent vanadium can be controlled, as a result the effectiveness that the worries about the maintenance by vanadium deposit etc. decrease is done so.

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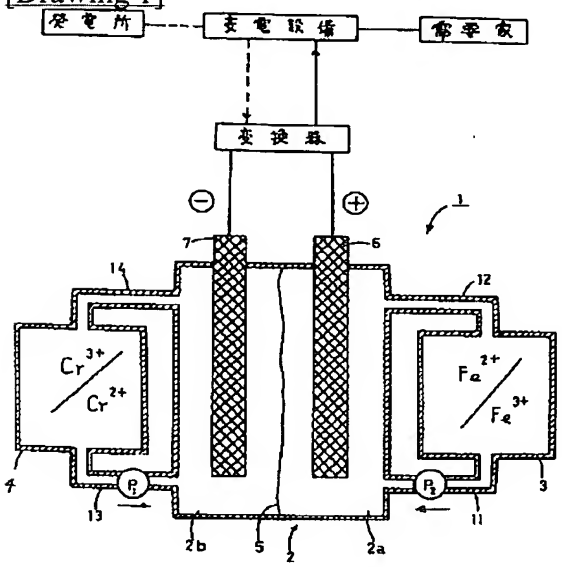
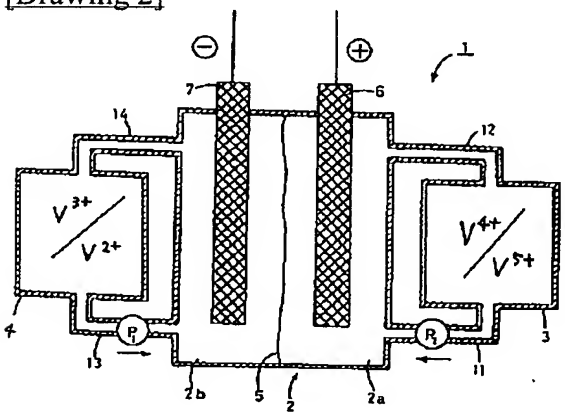
DRAWINGS

[Drawing 1]



[Drawing 2]



6：正極　7：負極

[Translation done.]